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| 1. REPORT DATE *(DD-MM-YYYY)* | 2. REPORT TYPE | 3. DATES COVERED *(From - To)* |
|---|---|---|
| | | |

**4. TITLE AND SUBTITLE**

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

**10. SPONSOR/MONITOR'S ACRONYM(S)**

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**

**12. DISTRIBUTION/AVAILABILITY STATEMENT**

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

**15. SUBJECT TERMS**

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | |
| | | | | | 19b. TELEPHONE NUMBER *(Include area code)* |

MOLECULAR BASIS OF ADHESION
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**Introduction and Motivation**

Adhesives are used in all areas of modern technology. Structural adhesives, or glues, bind materials together and provide mechanical strength. Paints and coatings protect critical surfaces from contamination and environmental exposure. The consequences of adhesive failure can range from the inconvenient, such as the peeling of paint, to the catastrophic, as in the failure of a critical mechanical component. In all cases, the performance of an adhesive bond is determined by molecular-level interactions at the interface between the two materials.

The investigation of the molecular basis of adhesive phenomena has been limited by three main factors. First, adhesion involves buried interfaces, requiring that any probe be able to access the location of the interactions of interest. Surface-specific techniques, such as atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), are unable to access the buried interface. The second problem is one of discrimination because molecules in the bulk of the material do not participate in the adhesive interactions. Lastly, because there are relatively few molecules at the interface relative to the bulk, any probe technique must be sufficiently sensitive. These challenges are overcome with the nonlinear optical method of vibrationally resonant sum-frequency generation (VR-SFG) spectroscopy.[1] The combination of interfacial spectroscopy and mechanical strength testing has great potential to improve our understanding of the molecular basis of adhesion.

**Summary of Significant Results**

Funding from AFOSR (YIP) commenced in March of 2009 and continued through May of 2012. We have published five papers[2-6] and submitted one other for publication[7] based on work supported at least in part by this funding. One doctoral student that was supported by this funding has completed his degree.[8] Portions of this work have been presented at six scientific conferences. The main accomplishments are summarized below.

Structure of Polystyrene Surfaces – A critical part of the investigation of adhesion is a correct understanding of the structure of polymer surfaces. One of the earliest polymers to be investigated with VR-SFG was polystyrene (PS).[9,10] Unfortunately, two different surface structures were reported for this material. A comparison of the two studies reveals important differences: different substrates for the thin films, different film thickness, and different annealing processes. It is possible that any or all of these factors would lead to different surface structures, and presumably different adhesion to the surface.
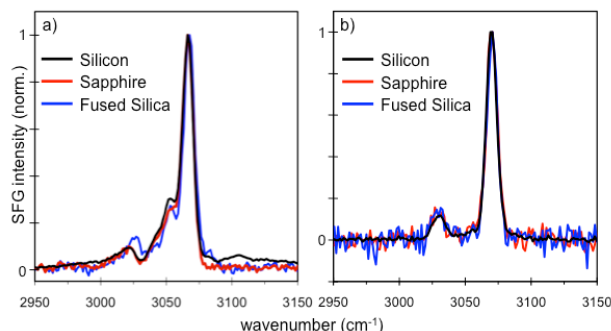


Figure 1. a) Normalized VR-SFG spectra (*ssp* polarization combination) of 90 nm PS on Si, sapphire, and fused silica. b) Same samples with full NR suppression. From Reference 2.

To resolve this discrepancy, we undertook a systematic investigation of how the structure of the PS surface depends on each of these parameters. We prepared 90 nm PS thin films on three different substrates: silicon wafers, fused silica windows, and sapphire windows. All annealed samples were processed in the same fashion (120°C for 2 hrs). Figure 1a compares the VR-SFG spectra of fresh, unannealed PS films on the three substrates. The differences in the spectra suggest that the surface structures may be different.

However, before we can state that there are definite differences in the surface structure, one key aspect of VR-SFG must be discussed. The VR-SFG intensity is typically modeled as

$$I_{SFG} \propto \left| \chi_{NR}^{(2)} + \chi_{R}^{(2)} \right|^2 = \left| \chi_{NR}^{(2)} + \sum_q \frac{A_q}{v_{IR} - v_q + i\Gamma_q} \right|^2 \tag{1}$$

where $\chi_{NR}^{(2)}$ and $\chi_{R}^{(2)}$ are the nonresonant and resonant nonlinear susceptibilities, respectively, and $A_q$, $v_q$, and $\Gamma_q$ represent the amplitude, center frequency, and half-width half-max linewidth, respectively, of a Lorentzian line shape of the resonant features. The sum is over all the normal vibrational modes of the molecules and $v_{IR}$ is the frequency of the IR beam.[1]

Because both the resonant and nonresonant terms are complex, they can interfere with each other. This is seen more clearly when equation (1) is expanded:

$$I_{SFG} \propto \left| \chi_{NR}^{(2)} \right|^2 + \left| \chi_{R}^{(2)} \right|^2 + 2\left| \chi_{NR}^{(2)} \right|\left| \chi_{R}^{(2)} \right| \cos\left[ \phi - \delta(v) \right] \tag{2}$$

where $\delta(v)$ is a frequency dependent phase term. Typically, the nonresonant SFG (NR-SFG) has been treated as a frequency independent background signal with constant amplitude that depends on multiple factors, such as the substrate material, visible wavelength, etc. We have shown, however, that such assumptions do not always hold true.[4] Interference between the resonant and nonresonant signal can allow for analysis of molecular orientations, although the nonresonant signal can often overwhelm the resonant signal, making spectra difficult to interpret.

Our VR-SFG system is based on a femtosecond laser, which produces a broad-band IR pulse. This allows us to probe multiple vibrational modes without scanning the IR frequency. Another advantage of broad-band systems is the ability to suppress the nonresonant signal by delaying the visible pulse relative to the IR.[11] (The spectra in Figure 1a were actually obtained with the NR signal suppressed to 90% of its value on a Au reference.) With full suppression of the NR signal, the three spectra become virtually identical, as seen in Figure 1b, suggesting that the surface structures are in fact the same, regardless of the substrate material.[2]

This ability to control the amount of NR signal in the VR-SFG spectrum has revealed some additional interesting features, both about the PS films and the spectroscopic technique. It has generally been assumed that the NR signal arises from the substrate and can therefore be treated as a background signal. We acquired VR-SFG spectra from three different 90 nm PS films on Si: a fresh sample and two additional samples, one that was annealed as described above, and one that was unannealed, but aged at ambient conditions for 1 week. See Figure 2. With full suppression of the NR signal, there is a
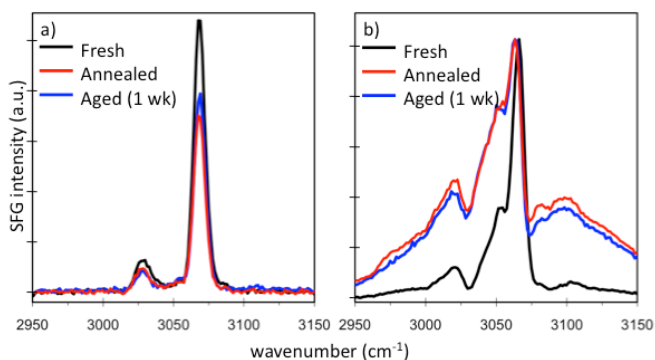
Figure 2. a) VR-SFG spectra of PS on Si with full NR suppression. Samples were fresh, annealed, or aged for 1 week. b) The same samples with NR signal present. Reference 2.

change in the overall amplitude, but not in the relative intensities, of the various resonant signals. When some NR signal is reintroduced, however, there are significant changes in the spectrum.[2] In particular, the amount of NR signal increases with annealing and aging. Thus, the NR signal is not merely a background that only depends on the substrate, but arises from the PS film itself and reflects the history of the sample. These results reinforce the necessity of measuring the parameters in Equation 1 experimentally rather than relying on complex data analysis.[2,12]

Refinements of VR-SFG – We initially thought the investigation of PS thin films would be a simple study. However, our results have forced us to revisit some of the common assumptions that have been made when analyzing VR-SFG spectra. In particular, the NR signal does not arise solely from the substrate and it should not be modeled as having a constant amplitude.[4] We have also shown that suppression of the NR signal affects the analysis of VR-SFG spectra. This happens because delaying the visible pulse apodizes the resonant free induction decay, leading to distortions in the lineshape and changing the relative intensities of the resonant features.[4] See Figure 3. Customary nonlinear curve fitting of VR-SFG spectra is inadequate, and we have developed an new approach that takes advantage of these time-domain aspects of VR-SFG to ensure that the parameters we determine are mathematically unique and physically relevant.[5]

Effects of Environment and Sample Handling – As discussed above, we have observed that the amount of NR signal changes with the handling of the PS thin films; aging and annealing lead to an increase in the NR signal.[2] We have also seen that the absolute intensity of the resonant signal decreases slightly after aging and annealing. According to the polymer literature, spin-coated thin films are typically annealed for considerably longer than the 2 hours that have typically been used in our and other spectroscopic investigations. We therefore annealed PS thin films for longer than 1 week, and observed a significant decrease in the intensity of the resonant signal. This suggests that samples subjected to long-term annealing have considerably more disorder in the surface structure than fresh samples or samples that are annealed for a short time.

We have also investigated the effects of surface modifications, such as plasma cleaning or exposure to UV radiation. It was previously reported that exposure to UV-ozone or oxygen plasma resulted in a decrease of the resonant VR-SFG signal, presumably due to disordering or degradation of the surface.[13] We subjected PS thin films on silicon substrates to 18 W RF plasma for only 1 second and observed a very different result. The resonant signal increased dramatically and the dominant feature shifted from 3069 cm$^{-1}$ to 3059 cm$^{-1}$, as seen in Figure 4.[6] This effect was only seen on conducting substrates, such as silicon and stainless steel, but was not seen on dielectric substrates, such as fused silica or sapphire. We have interpreted these results to indicate that, on conducting substrates, the electric fields between the substrate and the
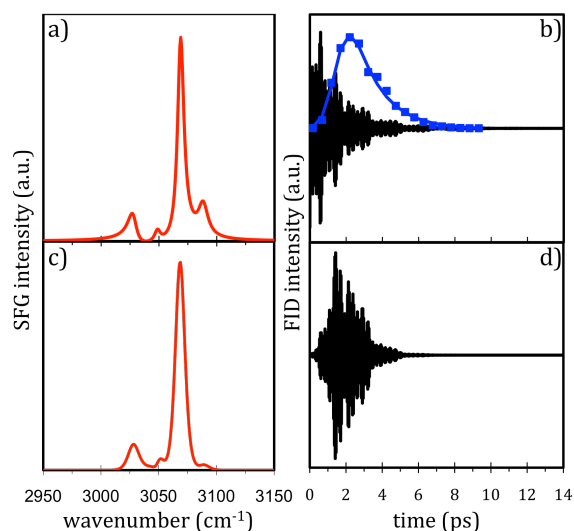


Figure 3. a) Simulated resonant spectrum with b) corresponding free induction decay (FID). The measured time profile of the visible pulse is also shown in b). Delay of the visible pulse c) alters the spectrum by d) apodizing the resonant FID. From Reference 4.

plasma lead to a preferential orientation of the bulk polymer. This breaks the local isotropy and allows for these phenyl groups to be detected by VR-SFG. This work is important for two reasons: it shows that plasma treatment can affect more than just the exposed surface, and that VR-SFG can detect molecules in sub-surface regions if the local isotropy is broken by sample processing. Annealing reverses much of this effect; the bulk-like response decreases and the spectra resemble those of untreated samples.[6]



Figure 4. PS thin film before and after plasma treatment. From reference 6.

This work has also led us to revise the vibrational mode assignments in the VR-SFG spectra of polystyrene surfaces.[7] Most significantly, we assign the band that is observed at 3059 cm$^{-1}$ to phenyl groups that exist in a sub-surface region of higher density.

Fabrication of Back-Surface Reference Materials – In order to properly analyze broad-band VR-SFG spectra, it is necessary to measure the profile of the IR pulse. This is typically accomplished with a reference material, such as a Au mirror. When investigating buried interfaces, it is desirable to have the reference material in the same physical location as the samples, thus a back-surface reference is needed. However, conventional Au mirrors use a Cr or Ti adhesion layer, making them unusable as back-sur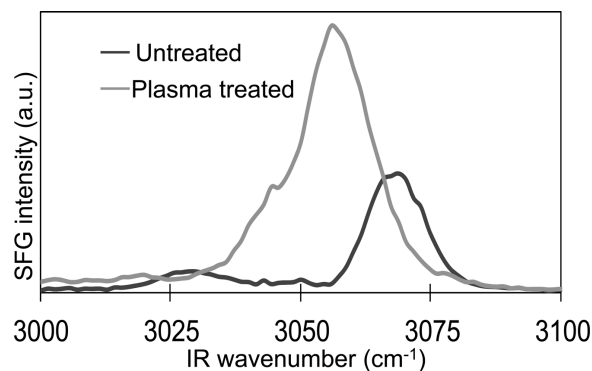face mirrors. We have developed back-surface mirrors that use 3-mercaptopropyltrimethoxy-silane (MCPTMS) as a non-metallic adhesion promoter.[3] These mirrors are robust and, more importantly, the MCPTMS monolayer does not cause any distortion in the reference measurements.

Strength Testing of Layered Polymers – We have also investigated the mechanical strength of layered polymers, with an initial focus on poly(methyl methacrylate) (PMMA) on PS. The purpose of the initial investigation was to establish testing protocols for bonded systems in general. The YIP funding allowed us to purchase an Instron model 3345 mechanical strength tester and we have developed initial protocols for tensile testing. We observed an interesting effect depending on the treatment of the layered samples. Samples were either annealed after both thin films were spin coated, or simply allowed to age under ambient conditions, with no annealing. We found that the strength to failure was not significantly different for the two sets of samples, but the quality of the separation between the two layers was different. As shown in Figure 5, annealed samples showed much cleaner separation between the PS and PMMA layers than the aged samples. This is likely due to the immiscibility of the polymers; annealing allows
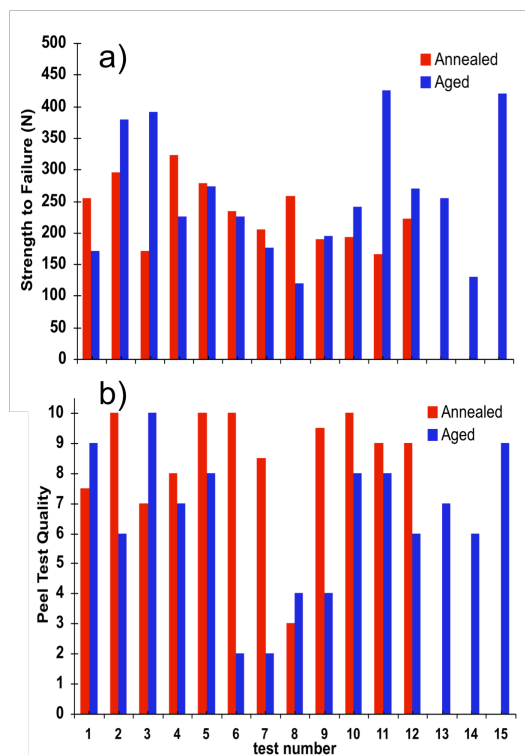


Figure 5. a) Strength to failure of annealed (232 ± 32 N) and aged (260 ± 62 N) samples. b) Quality of thin film separation. A score of 10 indicates clean separation.

for better phase separation of the two materials. Even with this clean separation, however, considerable force is required to pull the two layers apart. We are currently very close to coupling the strength testing apparatus to the spectroscopy system to probe layered samples while subjected to static and dynamic mechanical loads.

**Experimental Methods and Data Analysis**

The experimental methods are adequately described in the published manuscripts.[2-6] The Matlab code for processing variable time-delay spectra is included in Alexander D. Curtis's Ph.D. dissertation.[8]

**Executive Summary of Completed Dissertation**

Refining Vibrationally-Resonant Sum Frequency Generation Spectroscopy for Studies of Interfacial Interactions, Alexander D. Curtis – Analysis of vibrationally resonant sum-frequency generation (VR-SFG) spectra has relied on many assumptions. Some of these assumptions were experimentally checked and found not to hold true in certain cases. In particular, aspects of the nonresonant SFG signal have been identified that can lead to erroneous interpretations of VR-SFG spectra. New methodologies have been developed to acquire spectra and analyze them more accurately. These methods are based on time-domain considerations and have been demonstrated for the cases of polystyrene surfaces and octadecylsilane on fused silica.

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